

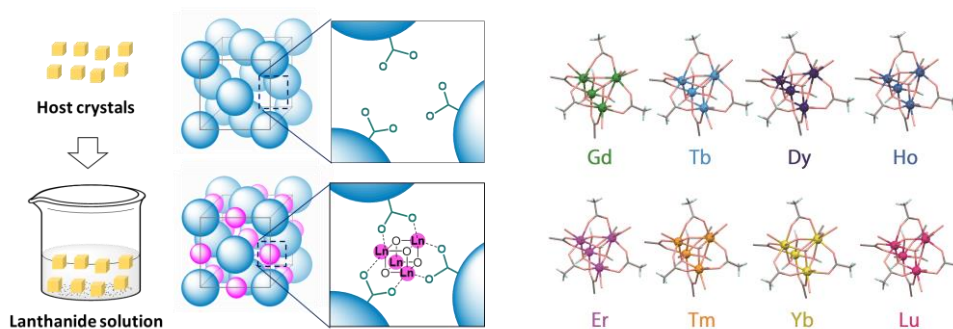
Creation of a series of lanthanide cubane clusters inside single-crystals of an anionic Rh_4Zn_4 complex with L-cysteinate

(¹Graduate School of Science, Osaka University) ○Nobuto Yoshinari,¹ Natthaya Meundaeng,¹ Takumi Konno¹

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The post-synthetic modification (PSM) of crystalline-materials has long attracted synthetic chemists and material scientists because it allows creating new compounds that are difficult to synthesize by conventional processes. Usually, such a solid-to-solid conversion needs a robust crystal lattice. Hence infinite materials, such as Zeolites and metal-organic-frameworks (MOFs), are widely explored as the host crystals. However, the PSM for the supramolecular crystals is relatively less explored due to their inherent instability. In this work, we report the creation of lanthanide cubane clusters inside a supramolecular crystal through PSM.¹⁾

As the host crystals, we employed the potassium salt of an octanuclear $\text{Rh}^{\text{III}}_4\text{Zn}^{\text{II}}_4$ complex anion with L-cysteine, $\text{K}_6[\text{Rh}_4\text{Zn}_4(\text{L-cys})_{12}\text{O}] \cdot n\text{H}_2\text{O}$.²⁾ Freshly prepared single-crystals of $\text{K}_6[\mathbf{1}]$ were immersed in an excess amount of $\text{Ln}(\text{OAc})_3$ ($\text{Ln} = \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Er}^{\text{III}}, \text{Ho}^{\text{III}}, \text{Tm}^{\text{III}}, \text{Yb}^{\text{III}}, \text{Lu}^{\text{III}}$) solution at room temperature. While the initial crystals $\text{K}_6[\mathbf{1}]$ were well-soluble in water, the resulting crystals $\mathbf{2}_{\text{Ln}}$ became insoluble in water with keeping single-crystallinity. Single-crystal X-ray analysis indicates that $\mathbf{2}_{\text{Ln}}$ involves cubane-type lanthanide hydroxide clusters, $[\text{Ln}_4(\mu_3\text{-OH})_4(\mu_2\text{-OAc})_3(\text{H}_2\text{O})_x]^{5+}$ and $[\mathbf{1}]^{6-}$ in a 1:1 ratio. Each lanthanide clusters are bound by three free carboxylate groups from $[\mathbf{1}]^{6-}$ through COO-Ln coordination bonds. As a result, the 3,3-connected **srs-b** type MOF structure is constructed. As far as we know, this is the first example of PSM from supramolecular crystals to MOFs by the installation of cationic species.



- 1) N. Yoshinari, N. Meundaeng, H. Tabe, Y. Yamada, S. Yamashita, Y. Nakazawa, T. Konno, *Angew. Chem. Int. Ed.* **2020**, *59*, 18048. 2) N. Yoshinari, S. Yamashita, Y. Fukuda, Y. Nakazawa, T. Konno, *Chem. Sci.* **2019**, *10*, 587.